T-Shaped Fluorophores Towards the Development of Novel Fluorescent Architectures

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Abstract

This study reports the synthesis and photophysical characterization of 12 novel compounds from two new fluorophore architectures, in order to study the photophysics of cruciforms in relation to stilbenes. Therefore, analogues of cruciforms missing a styryl or arylethynyl branch were synthesized. The response of some of these T-shaped fluorophores to metal salts and protons in CH_2Cl_2 was studied. Likewise, the solvatochromicity of all derivatives was studied. The derivatives lacking a distyrylbenzene moiety were found to be photochemically unstable and possessed characteristics similar to stilbenes. Derivatives containing a distyryl branch were found to be photochemically stable, with responses analogous to cruciforms.

Introduction

Conjugated organic molecules have attracted interest as fluorescent sensors and compounds in organic electronic devices. Chromophore design targets materials with electronic and optical properties necessary for complex applications. Therefore, when developing optoelectronic devices, it is advantageous to design materials on a molecular level in order to engineer necessary optical properties for device integration. With such materials, for the chromophore to display a ratiometric sensory response, the analyte must interact with the chromophore in a way that changes the chromophore's HOMO-LUMO gap. In most materials however, the dye-analyte interaction causes nearly equal shifts of the HOMO and LUMO orbitals, causing little or no change to the HOMO-LUMO gap.[1] In other words, the absorbance and emission of the fluorophore does not significantly change upon analyte interaction. Thus, materials that show disproportionate HOMO-LUMO shifts upon analyte interaction hold promise towards the development of novel devices.[1]

In the field of conjugated organic materials, initially compounds were developed as one-dimensional 'molecular wires'. This architecture shows spatially congruent FMO

structures.[2] Due to the spatial congruence of the FMOs in 'molecular wires' it is difficult to elicit a change to one FMO without affecting the other. One strategy to circumvent the shortcoming of these one-dimensional compounds is to design molecular architectures which possess spatially separated FMOs. This can be accomplished by the development of two-dimensional materials which use orientational factors to impede the electronic interaction between discrete one-dimensional subunits.[2] Essentially, because of the localization of the HOMO and LUMO to separate one-dimensional subunits, the interaction of an analyte along one axis may only significantly affect one FMO; this causes the wavelength of the absorbance and emission of the fluorophore to shift.[1]

However, the usefulness of fluorophores extends beyond FMOs; the fluorophore must be photochemically stable. Photochemically unstable molecules are not useful, as the photochemical reaction products lead to changes in the absorbance/emission of the bulk solution. These changes are unrelated to dye-analyte interaction. In cases of photochemical instability, differences in absorbance or emission cannot be attributed to the analyte being studied. One example of a class of fluorophores which suffers from photoinstability is stilbenes. Stilbenes are known to photoisomerize between the *E* and *Z* isomers in the presence of ultraviolet light.[3] Likewise, stilbenes undergo photooxidative cyclization in the presence of molecular oxygen to form phenanthrenes.[4]

Therefore, in order for a fluorophore to be useful as a chemical sensor, it must show disproportionate HOMO-LUMO shifts upon analyte interaction; as well, the fluorophore must be photochemically inert. Various two dimension fluorophores investigated for device integration which embody these properties include spiro compounds[5], paracyclophanes[6], tetraethynylethenes[7], tetrasubstituted tolanes[8],

cruciforms[9], etc[10]. These compounds have been used to sense targets such as metal ions[9], amines,[11] chemical warfare agents[12], explosives[13], and bacteria[14].

While there are a handful of fluorophore architectures, the investigation of new architectures is necessary to progress the field. Each architecture has unique photophysical properties which are useful for specific applications. As well, the study of each architecture sheds light upon how structure impacts molecular photophysics.

This study reports, the design, synthesis and characterization of two novel fluorophore architectures, 2-styryl-1,4-di(phenylethynyl)-benzenes (stilbeneoid-T-shapes, STSs) and 2-(phenylethynyl)-1,4-distyrylbenzenes (distyrylbenzeneoid-T-shapes, DTSs). To investigate these new architectures, twelve DTS and STS derivatives were synthesized and their acidochromic and metallochromic responses were studied. Additionally, the photochemical stability of these novel fluorophores was determined. The purposes for this investigation are manifold. First, this research introduces two new fluorescent architectures and studies their suitability for device integration. Additionally, these new compounds serve as a probe to determine what conformational factors cause stilbene and cruciform fluorophores to be photochemically and photophysically different, while maintaining the same base architecture.

This research is useful, beyond the characterization of two new fluorophores, for the development of new optoelectronic devices. By rigorously studying the photophysical and photochemical consequences of modifying the one-dimensional subunits which compose two dimensional architectures, future researchers will have a greater ability to intelligently design new fluorophores.

STS's and DTS's are a structural off-shoot of the cruciform architecture. STS's differ from cruciforms in that they lack one styryl branch, while DTSs differ in that they have only one arylethynyl branch. In this way, the cruciform architecture has been dissected to analyze how modification of the 1-D subunits which compose cruciforms affects molecular photophysics.

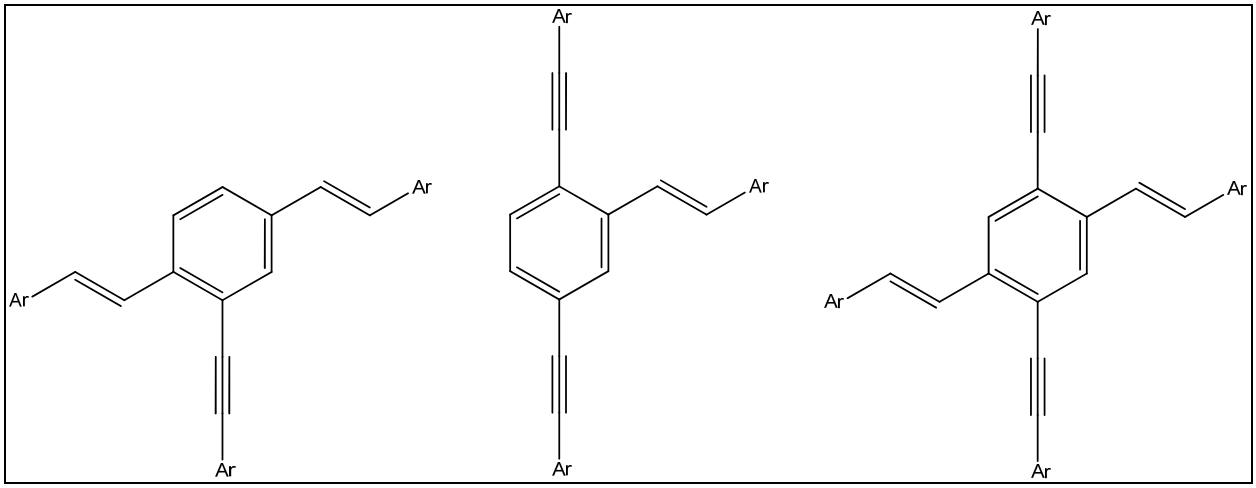


Figure I: This figure demonstrates the structural similarity of DTSs (left) STSs's (middle) and cruciforms (right).

Although cruciforms have been extensively studied and their photophysics have been rigorously characterized, it is not fully understood why the specific conformation of 1-D subunits in cruciforms has led them to be such versatile fluorophores. Cruciforms demonstrate ratiometric responses to many analytes including protons[15], metals[16] and various amines[11]. As well, cruciforms show very high quantum yields.[17] Another, very important property of cruciforms is that they are photochemically stable. Despite these many favorable properties, cruciforms were not intelligently designed; they are a product of serendipity. Cruciforms were only studied as fluorophores to probe the anomalous photophysics of PPV polymers containing a PPE crosslinker.[1].

Cruciforms are conformationally highly substituted stilbenes, and were expected to have photophysical properties similar to stilbenes; however, their photophysical properties were found to greatly different. While the electronic properties of cruciforms are currently well understood, it still remains unclear why certain 2D functionalized stilbene derivatives conserve the general FMO structure of simple stilbenes while other 2D functionalized stilbenes (cruciforms) adopt FMO conformations which are vastly different. The unintended discovery of cruciforms as useful fluorophores shows that it is necessary to go beyond simply characterizing a new architecture, but investigate how the architecture's structure impacts photophysics.

Methods

In order to fully study these new fluorescent architectures, seven STSs and five DTSs were synthesized. All T-shaped compounds which were synthesized had substitution patterns analogous to cruciforms studied in this lab.

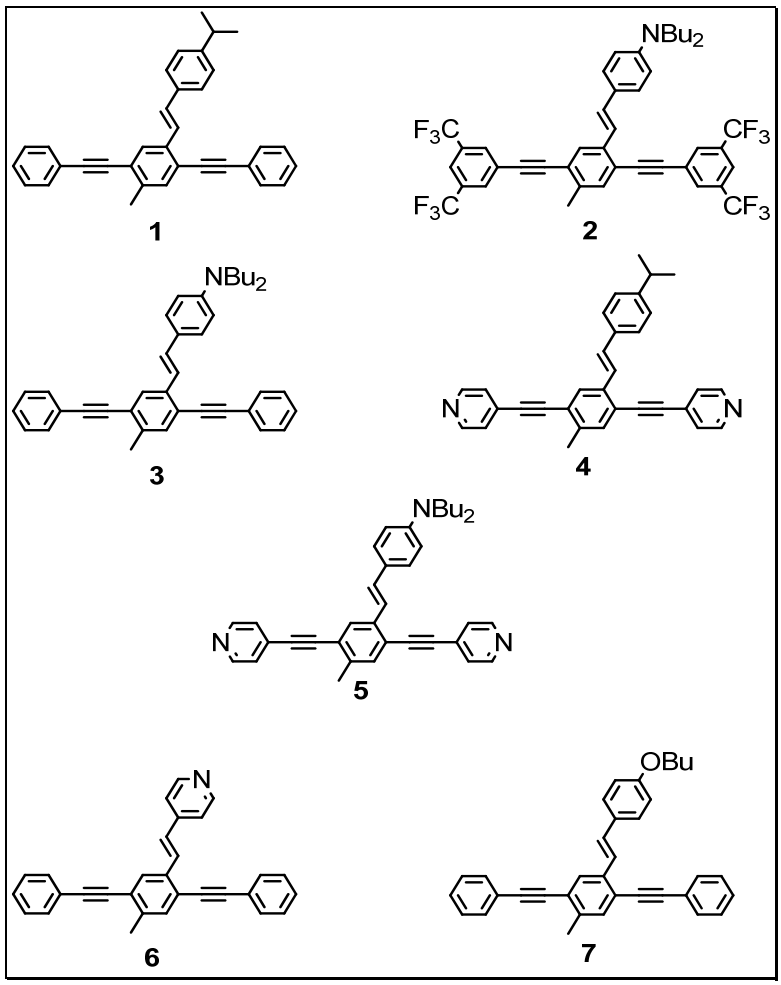


Figure II: Depicted are the STS class compounds synthesized for this study.

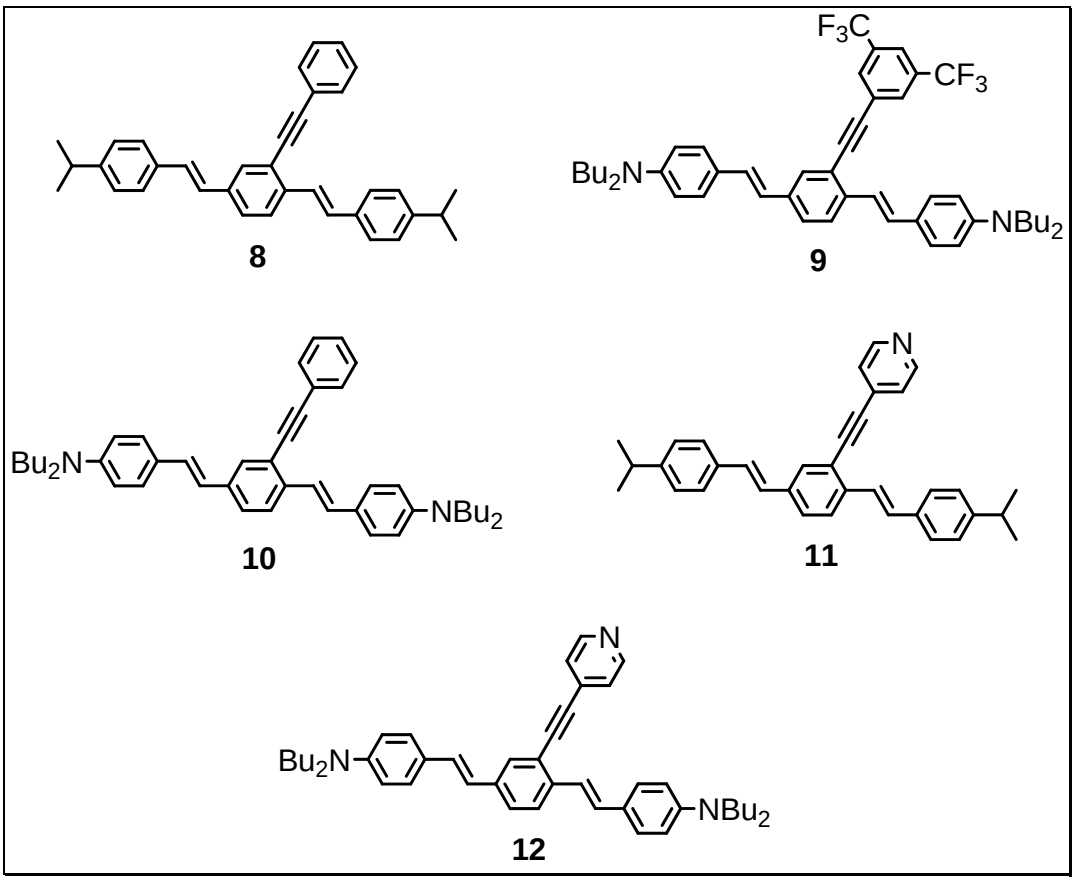


Figure III: Depicted are the DTS class compounds synthesized For this study.

The precursor for all STS compounds was monopohophonate **P1** which was prepared by di-iodination of p-xylene followed by benzylic bromination with molecular bromine in AcOH and finally phosphonated via the Arbuzov reaction. STS compounds were prepared from this precursor via Horner reaction with the functionalized benzaldehyde followed by Sonogashira coupling with the proper phenylacetylene.

The precursor for all the DTS compounds was diphosphonate **P2**, which was prepared via the literature procedure from p-xylene.[1] All DTSs except **9** were prepared from **P2** by a Horner reaction followed by Sonogashira coupling. For **9** however, the distyrylbenzene failed to give acceptable yields via Sonogashira coupling with 4-

ethynylpyridine; therefore, **9** was synthesized via Songashira coupling followed by a Horner reaction.

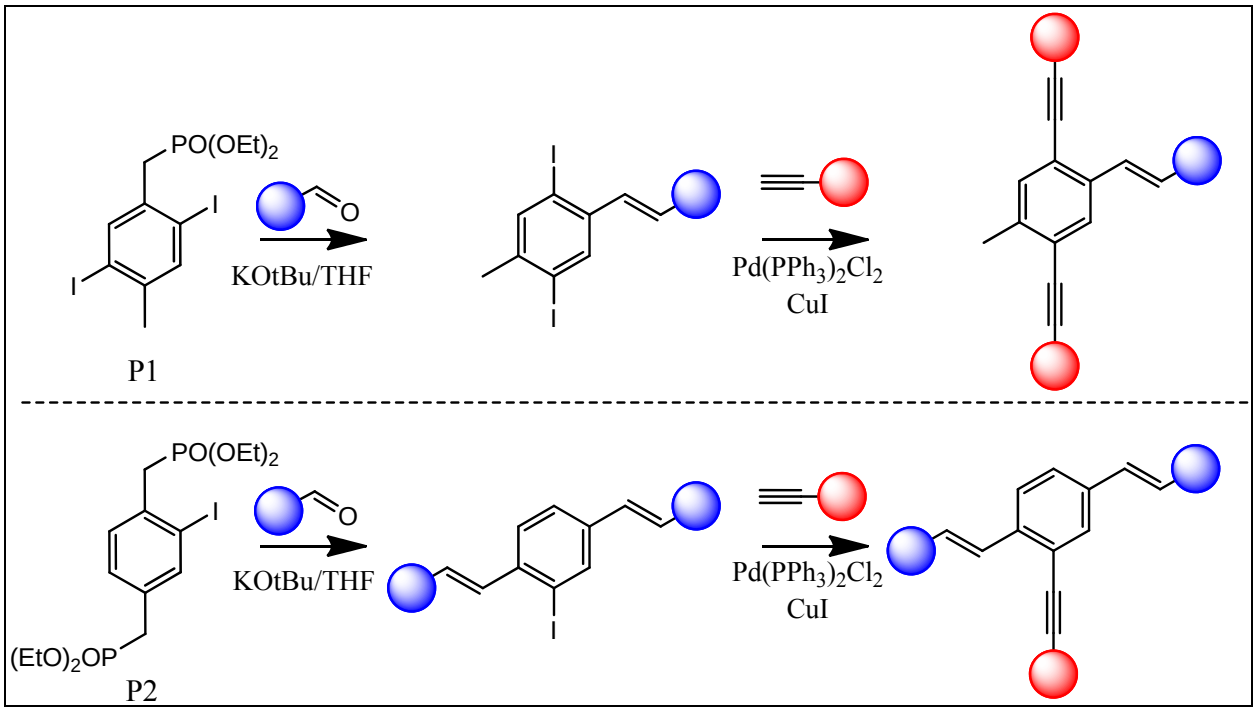


Figure IV: A diagram indicating the overall synthetic scheme for the preparation of STSs (top) and DTSs (bottom) is depicted.

All aldehydes used in this study were commercially available and used without further purification. Phenylacetylene was the only commercially available alkyne used in this study, all other alkynes were prepared from the corresponding bromo compounds via Sonogashira coupling with either TIPS-Acetylene or TMS-Acetylene. These protected alkynes were deprotected either *in situ* or *ex situ* to yield the arylacetylene.

All spectroscopic studies of these compounds were conducted in spec. grade solvents at ca.1 mg/mL dye concentrations. Metal and acid response studies were conducted in methylene chloride. The acid used in all studies was trifluoroacetic acid.

All metal sensing studies were conducted using saturated solutions of the metal triflate in methylene chloride.

The excitation frequency used for the emission studies was always 10 nm greater than the peak absorbance. For compounds which exhibited two absorbance maxima, the excitation wavelength was selected to be 10 nm less than the lowest energy absorption maximum.

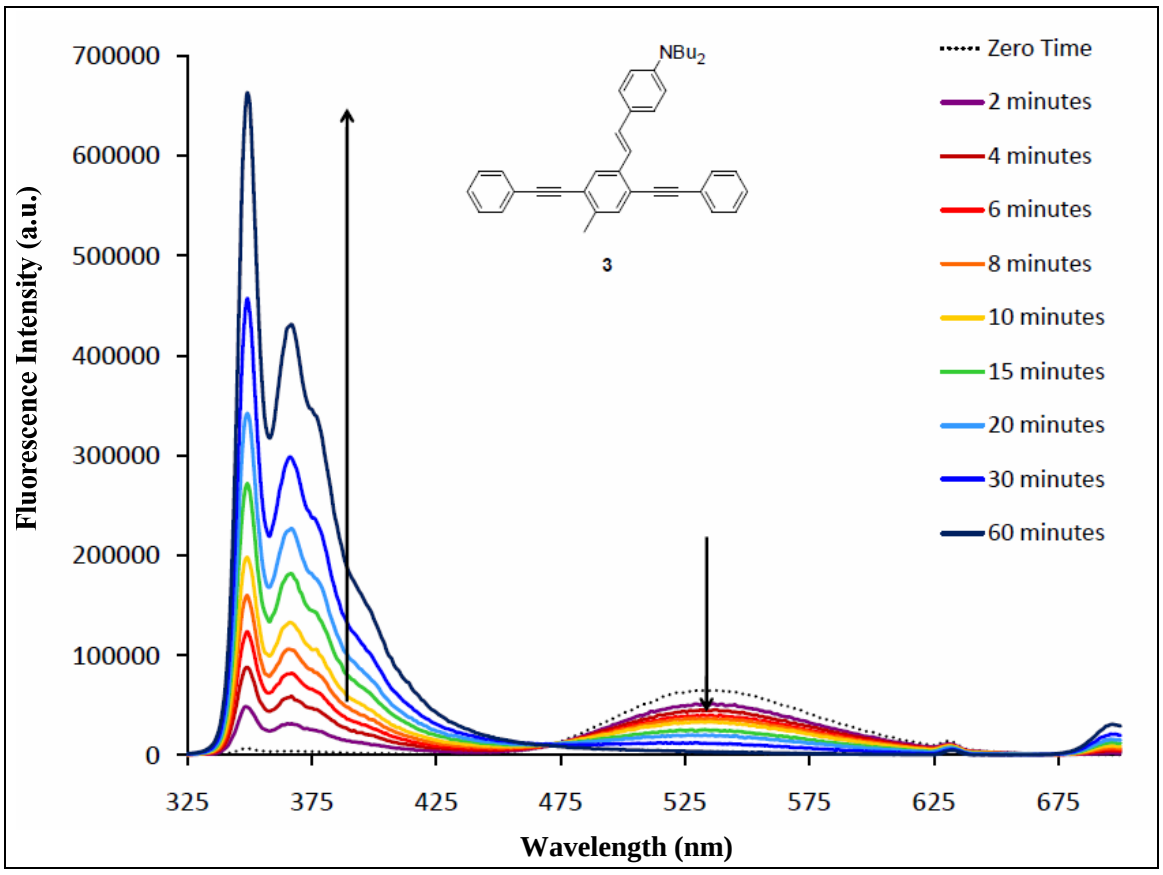
Results and Discussion

All derivatives of the STS compounds were found to be photochemically unstable. For this reason, only solvatochromic studies of the STS compounds were completed. It must be understood that, while the materials used in these studies were shown to be of high purity by all metrics, in the process of preparing the many stock solutions used in this study the dye may have degraded from exposure to environmental UV radiation.

A spectroscopic investigation of the photochemical degradation of the STSs was undertaken with compound **3** in methanol. This study showed that after an hour of irradiation by the fluorimeter, the dye had quantitatively degraded. This was indicated by nearly no fluorescence at the λ_{max} of the dye by the end of the experiment and the appearance of a new emission band at ca. 550 nm.

An H^1NMR experiment was conducted to determine the reaction product of the photochemical degradation of compound **3**. The solvent which showed the most rapid degradation of the STS compounds was methanol. Therefore, an aliquot of **3** dissolved in methanol-d_4 was irradiated by a UV light source (λ_{max} 365 nm) overnight. The

experiment was conducted such that the dye solution was allowed to interact with atmospheric oxygen.



*Plot I: The results for the spectroscopic study of the photochemical degradation of compound **3** in methanol is depicted.*

The NMR results of this experiment were not conclusive primarily due to a low solubility of **3** in methanol. However, singlets in the region characteristic of benzaldehydes were noted. This indicates that the stilbene moiety of the STS compounds is probably photo-oxidatively cleaved by molecular oxygen, generating two benzaldehydes. However, the red shift of fluorescence after exposure to UV light indicates the situation may be more complicated. The product from cleavage of the stilbene would be expected to be blue fluorescent. Therefore, further studies are being conducted to attempt to identify the products of this degradation. Despite the instability

of the STS compounds, it must be noted that these compounds were found to be stable on the timescale of weeks when stored in a refrigerator in the absence of light.

The fluorescence studies of the STS compounds in a variety of solvents showed that the dibutylaminophenyl functionalized STS derivatives displayed a high degree of solvatochromism. Other STS derivatives were unremarkable. Compound **2** and **5** are particularly interesting, showing a wide range of emissions depending upon the solvent. This range of emissions is likely due to charge transfer. Charge transfer is indicated by the striking red shift in polar solvents. Compound **5** exhibited equally remarkable solvatochromicity in conjunction with spectral features indicating the possibility multiple charge transfer bands.

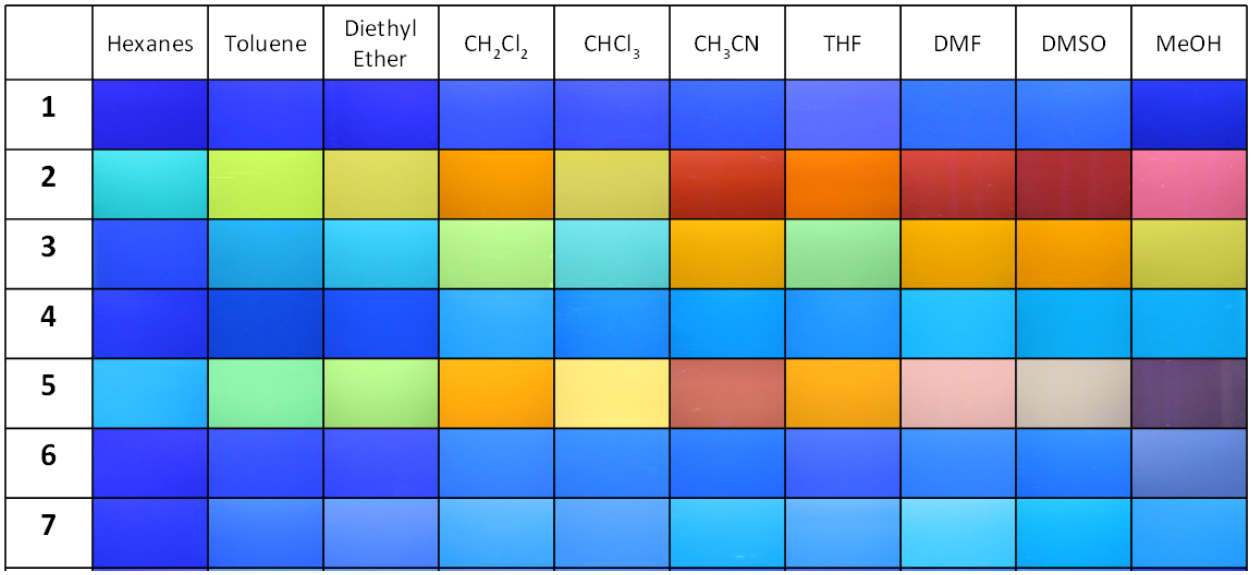
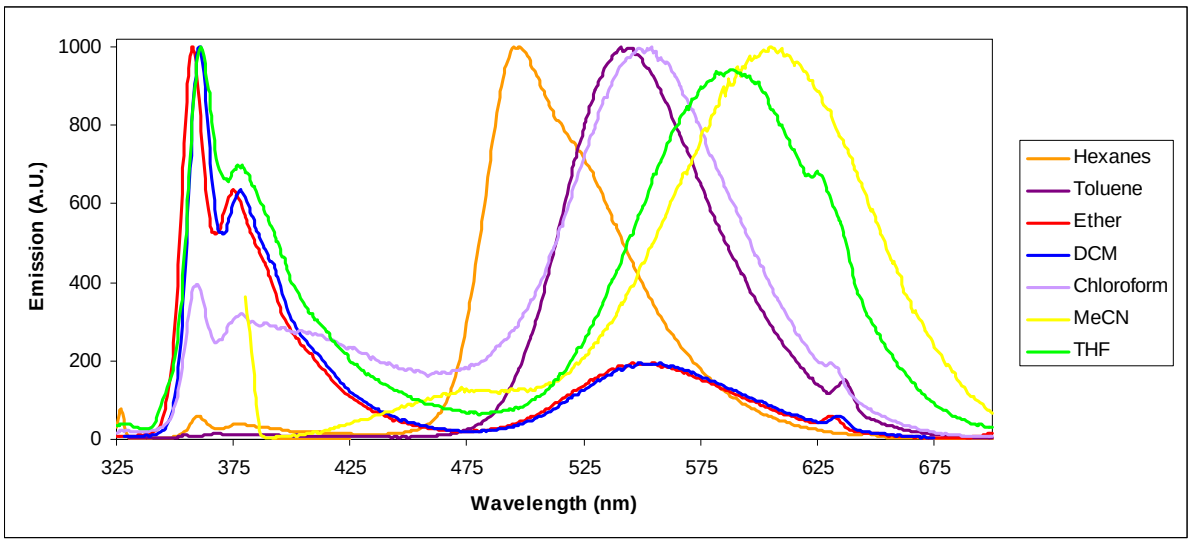


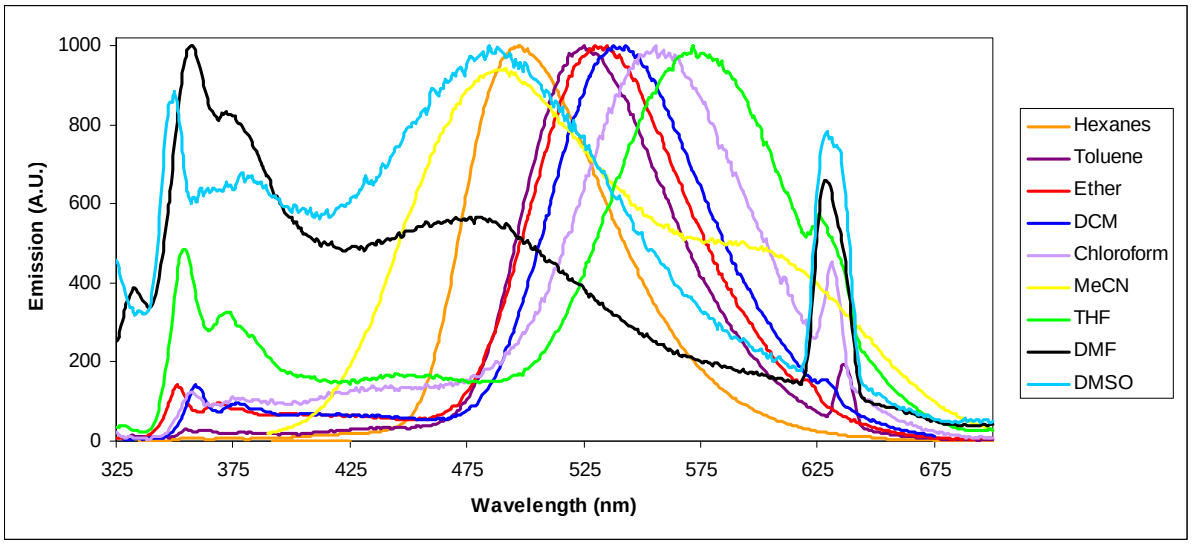
Figure V: Tabulated is a chart showing the color as obtained by a photograph of fluorescence of each STS compound in each solvent studied.

Quanitatively, the STS compounds generally showed similar absorbance maximums, at ca. 320 nm, despite fictionalization. The donor-acceptor substituted STS compounds showed a high degree of solvatochromicity. Compound **2** exhibited a 300 nm

shift in emission max throughout the range of solvents studied. Compound **5** was equally remarkable, but showed a shoulder in many of its emissions indicating the possibility of multiple charge transfer bands.

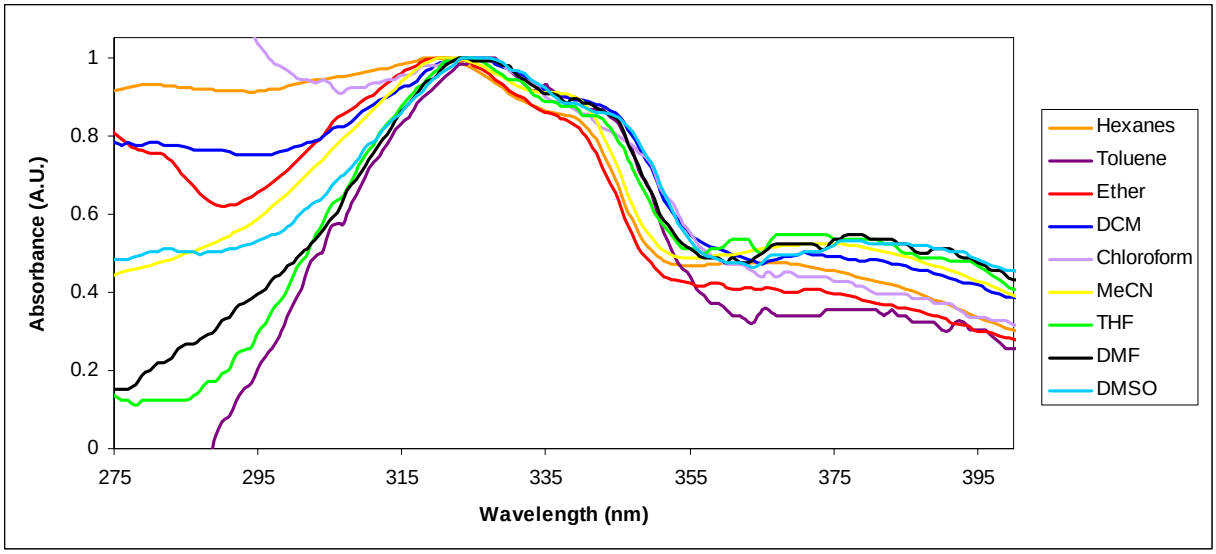


*Plot II: The normalized emission spectra of compound **2** in various solvents are plotted.*

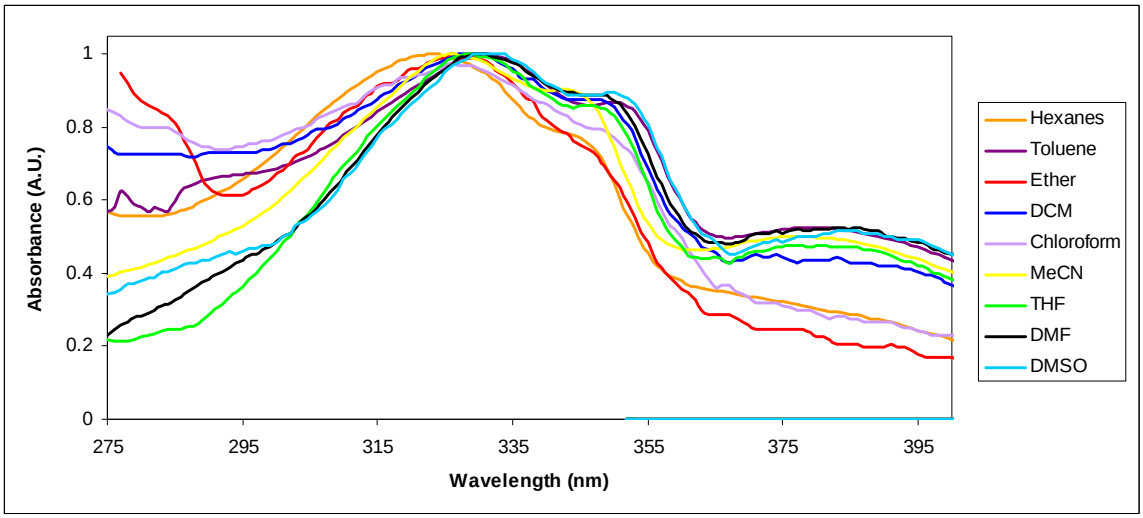


*Plot III: The normalized emission spectra of compound **5** in various solvents are plotted.*

One interesting aspect of the absorbance spectra of the STS compounds is that generally only one absorption band is noted. Cruciforms and other 2-D fluorophores generally exhibit two absorption bands arising from each axis of the molecule. In the case of STS molecules, it is possible that the arylyethynyl moiety has an absorbance very close to that of the stilbene moiety. This would explain the very broad absorbance peaks of these compounds. A more likely possibility however is that the arylethynyl moiety absorbs at very low wavelengths, outside the range of the study conducted. No matter the cause, this feature is unique to the STS derivatives and is in stark contrast to the cruciforms and DTS compounds.



*Plot IV: The normalized absorbance spectra of compound **5** in various solvents are plotted.*



*Plot V: The normalized absorbance spectra of compound **2** in various solvents are plotted.*

The solvent studies of the DTS compounds, showed the most solvatochromic derivatives to be those with a dibutylaminophenyl substituted styryl axis. The donor-acceptor substituted compounds showed the greatest degree of solvatochromicity, no doubt due to charge transfer bands. The color of fluorescence of the DTS compounds was extremely similar to those of the corresponding cruciform analogs.[15]

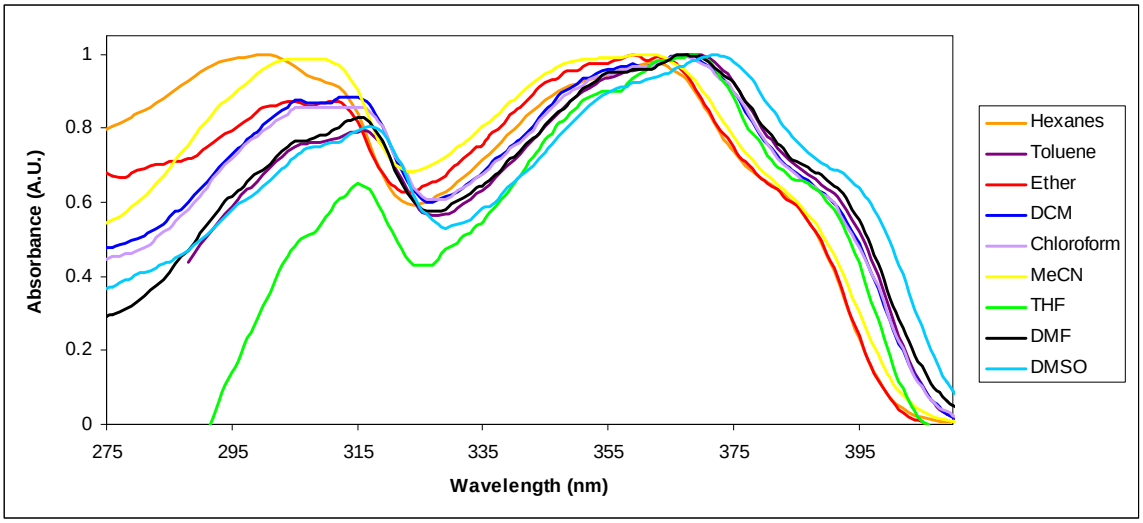
	Hexanes	Toluene	Diethyl Ether	CH_2Cl_2	$CHCl_3$	CH_3CN	THF	DMF	DMSO	MeOH
8										
9										
10										
11										
12										

Figure VI: Tabulated is a chart showing the color as obtained by a photograph of fluorescence of each DTS compound in each solvent studied.

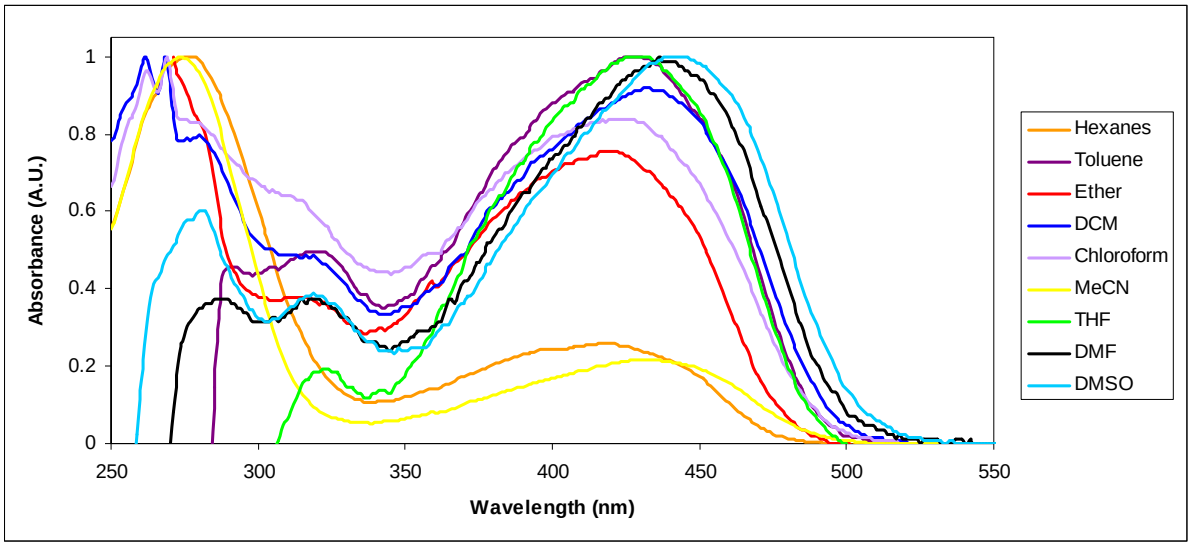
The absorbance spectra of the DTS compounds are much more variable than the STS compounds. In general, the dibutylaminophenyl substituted DTS compounds had lower energy absorptions than the isopropylphenyl substituted analogs. Likewise, for each compound within the range of solvents tested, the DTS compounds showed a greater variability in the wavelength of absorption. These absorption characteristics are similar to cruciforms.[18]

The emission spectra were as well very similar to cruciforms. Certain compounds showed a vibronic progression; this indicates short lived discrete transitions between various excited states and ground state. The emission spectrum of compound **8** is representative of this phenomenon.

Another aspect of the absorbance spectra which is cruciform-like, is the appearance of two absorbance bands. One band arrises from the distyryl axis of the molecule, while the other band arises from the arylethynyl axis.[1] This aspect of the absorbance spectra of the DTS compounds is unique with respect to the STS compounds, but shared with the cruciforms.



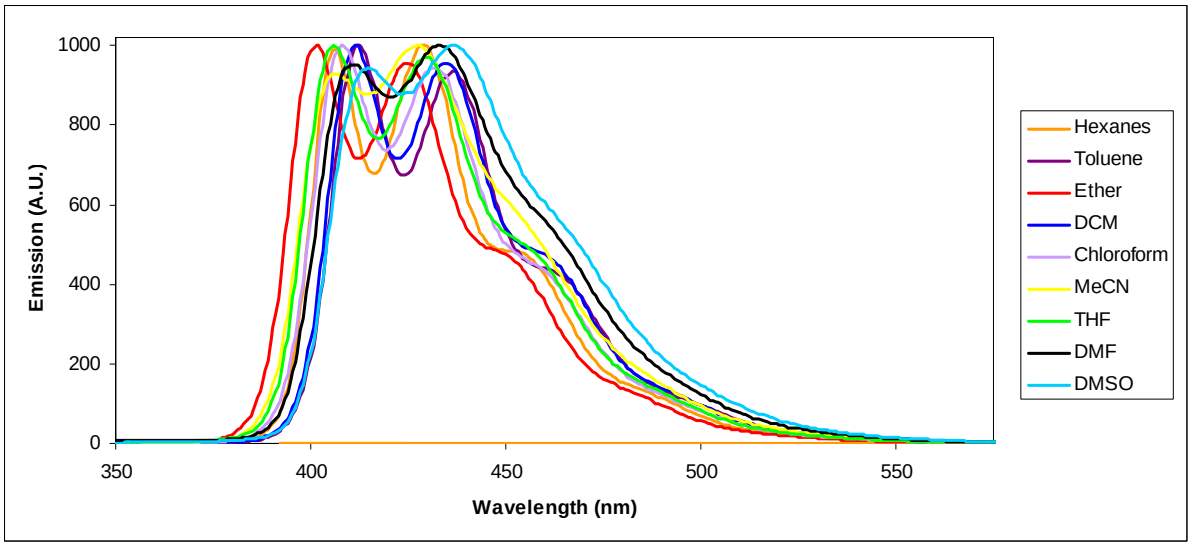
*Plot VI: The Absorbance spectra of compound **8** in various solvents are plotted.*



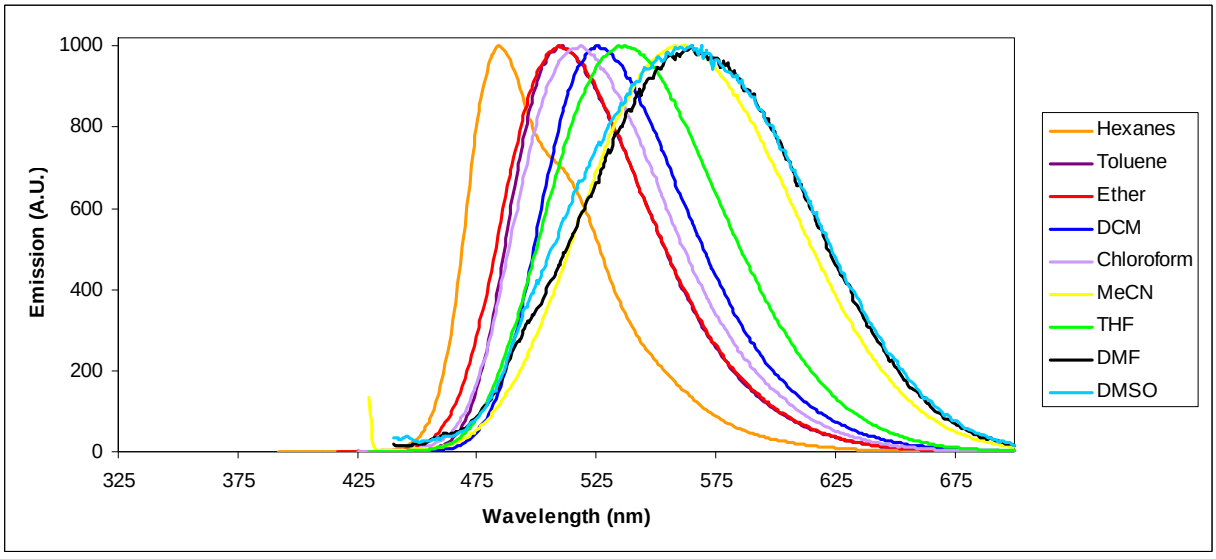
*Plot VII: The Absorbance spectra of compound **9** in various solvents are plotted.*

Like the cruciforms, donor substituted DTSs show charge transfer bands in their emission spectra.[18] Compound **9** is a prototypical example, showing the red-shifted emission of the charge transfer species as well as the higher energy emission of the non-charge transfer species. With increasing solvent polarity, the charge transfer species peak increases in intensity with the concomitant decrease in intensity of the non-charge transfer peak.

The degree of solvatochromistm exhibited by the DTS compounds is less than that of the STS compounds. The range of absorbance maxima exhibited by these compounds is in accordance with those of the cruciforms.[19]



*Plot XVIII: The emission spectra of compound **8** in various solvents are plotted*



*Plot IX: The emission spectra of compound **9** in various solvents are plotted*

The metal sensing studies of selected DTS compounds showed these compounds were unresponsive to the alkali metal ions. Compounds **9** and **11** showed red shifts in the presence of Mg^{2+} while **10** and **12** showed blue shifts. None of the dyes exhibited response to calcium. All dyes showed good response to Zn^{2+}, Mn^{2+}, Cu^{2+} and trifluoroacetic acid. Dyes **9** and **10** were blue shifted upon interaction with these species. No doubt, this is due to interaction with analyte causing removal electron density from the amine functionality effectively reducing its electron donation to the fluorophore moiety of the molecule. Dyes **11** and **12** show red shifts in response to these analytes; for **11** the red shift is simply due to co-ordination of the pyridyl moiety with the analyte, imparting increased efficiency as an electron acceptor. The case with **12** is more complicated, as the analytes are increasing the acceptor character of the pyridyl group while decreasing the donor character of the dibutylamino group; therefore, a red shift from one interaction and a blue shift from the other. The overall response is a red shift, the degree of which is less than that of compound **11**.

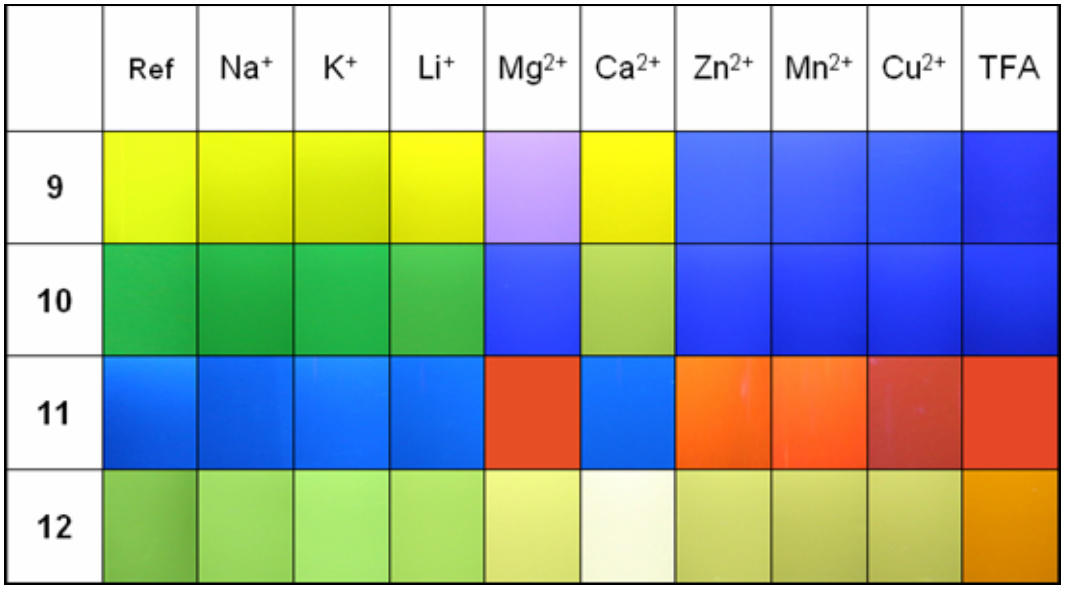
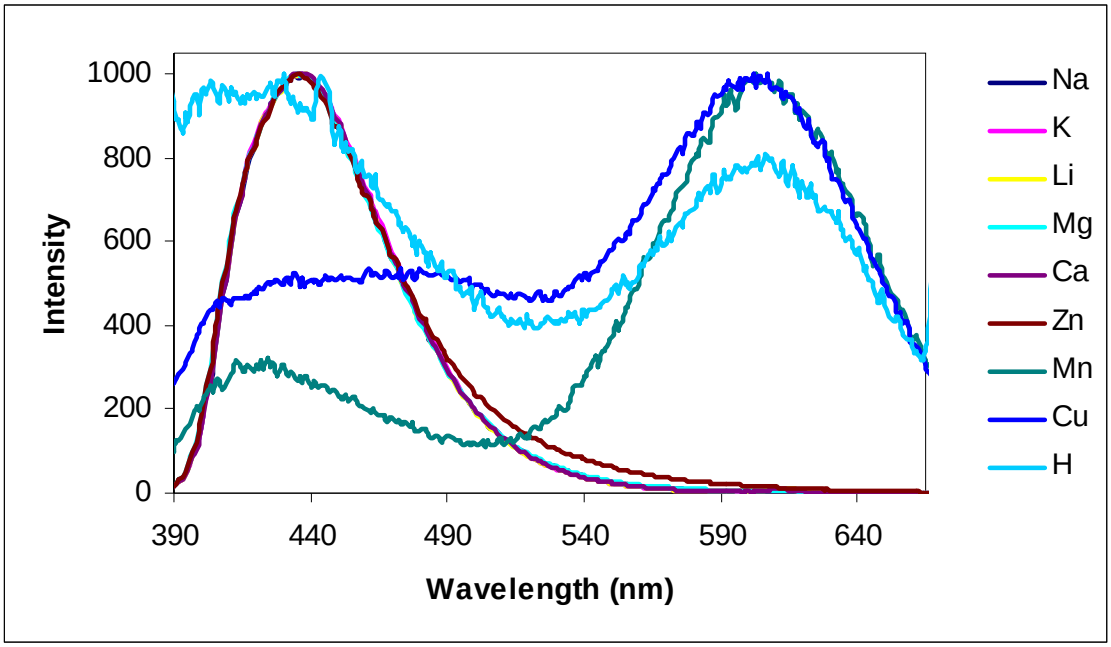
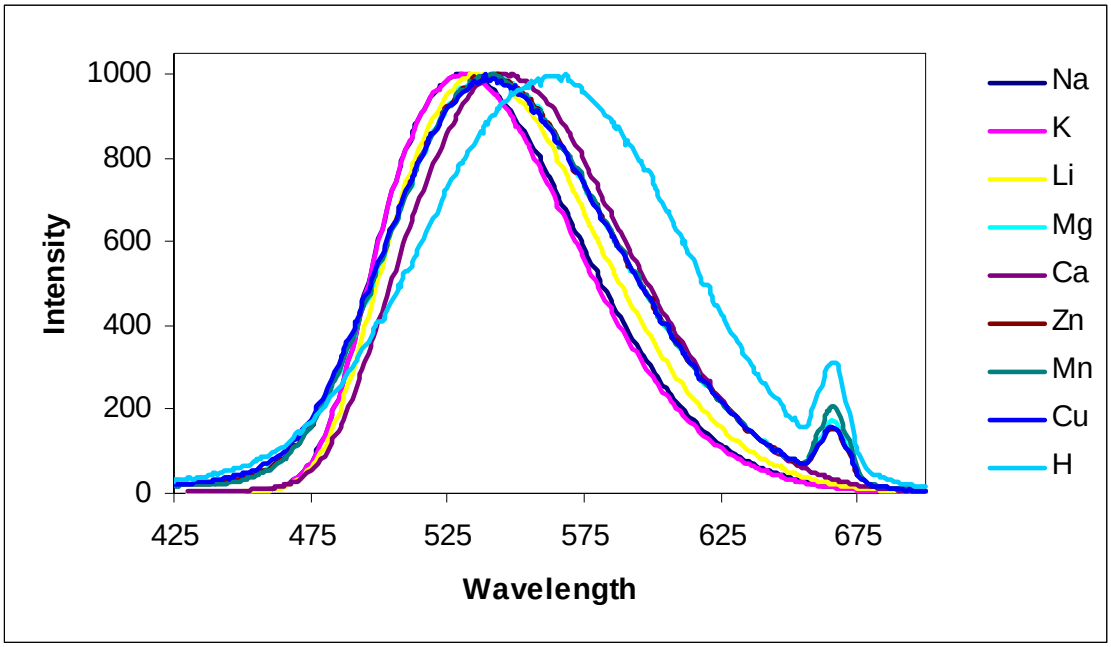


Figure VII: Tabulated are photographs depicting the fluorescence of each DTS compound in the presence of the metals studied.

Spectroscopy showed that interaction with the analytes caused both shifts in the absorbance and the emission of each dye. The alkali metals showed absorbance and emission spectra which are very similar to the native compound. In general, absorption at lower energies caused emission at lower energies. Overall, the spectra of these compounds is unremarkable and very similar to those of the cruciforms.[15]



*Plot X: The emission spectra of compound **11** in various solvents are plotted*



*Plot XI: The emission spectra of compound **12** in various solvents are plotted*

Conclusion

Overall, while the STS compounds showed surprising solvatochromicity, they lacked the necessary photochemical stability to be useful for device integration. The DTS compounds on the other hand were stable and spectroscopically similar to cruciforms.

The great solvatochromicity of the STS compounds is very stilbene like.[20] As well the small change in absorbance but great change in emission wavelength is a stilbene characteristic.[20] With these stilbene characteristics, comes a great disadvantage. Like stilbenes, the STS compounds are photochemically unstable.

The DTS compounds, by nearly every metric are very cruciform like, both qualitatively and quantitatively. The vibronic progressions of the non-donor-acceptor substituted DTSs and great changes in absorption maxima in different solvent/metal

environments are akin to cruciforms. As well, the photochemical stability of these compounds is shared with the cruciforms.

Therefore, it appears that the main characteristic which distinguishes stilbenes from cruciforms is the distyrylbenzene moiety. Distyrylbenzene functionality not only appears to confer robustness to the molecule but also confers the properties which give cruciftorms and DTSs their unique photophysics. This is supported by the very similar photophysics of these compounds, despite the lack of a second arylethynynl branch.

Overall, the STS compounds are unsuitable for device integration. The DTS compounds on the other hand are interesting fluorophores that do merit further research. As it stands however, there appears to be no specific benefit of the DTSs over their cruciform cousins.

With respect to understanding the photophysical relation of these compounds, the T-shapes have been invaluable towards highlighting what conformational differences separate cruciform-like compounds from stilbene-like compounds.

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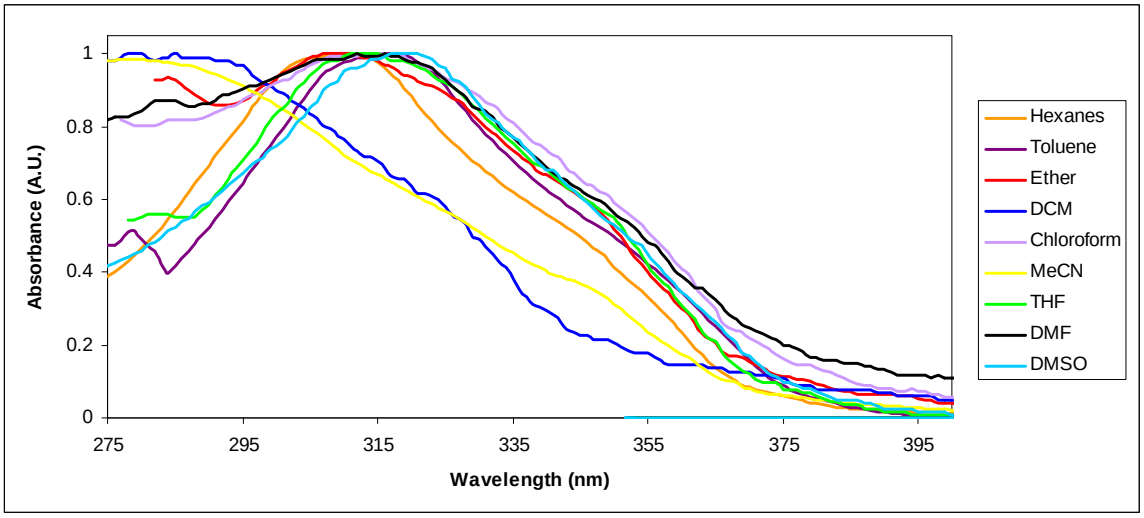
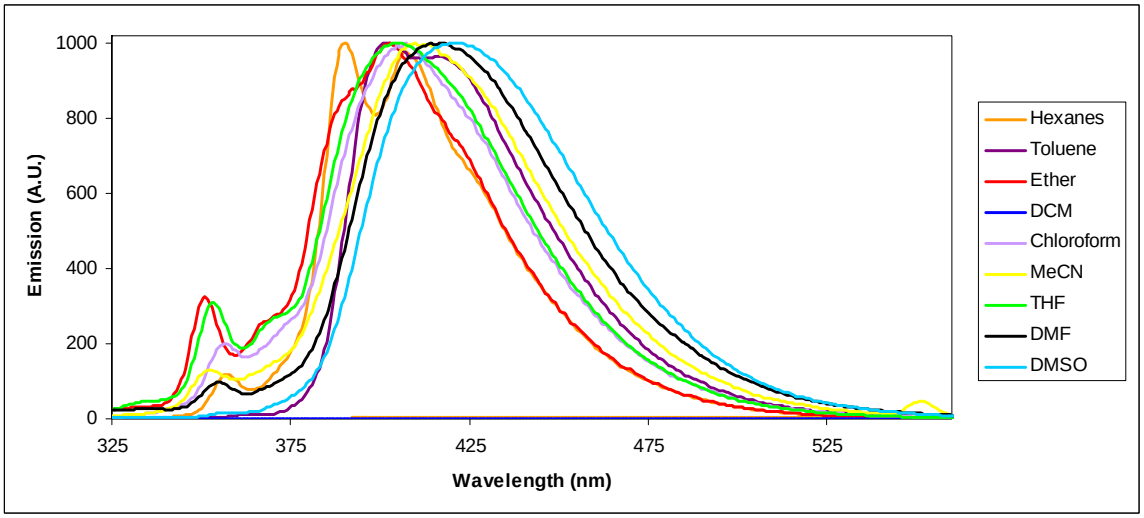
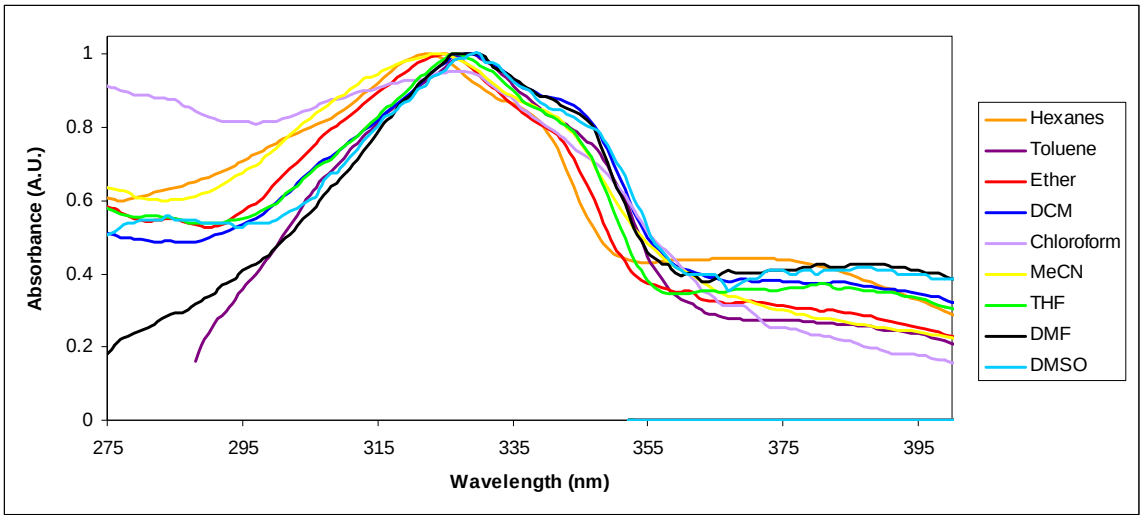
Appendix



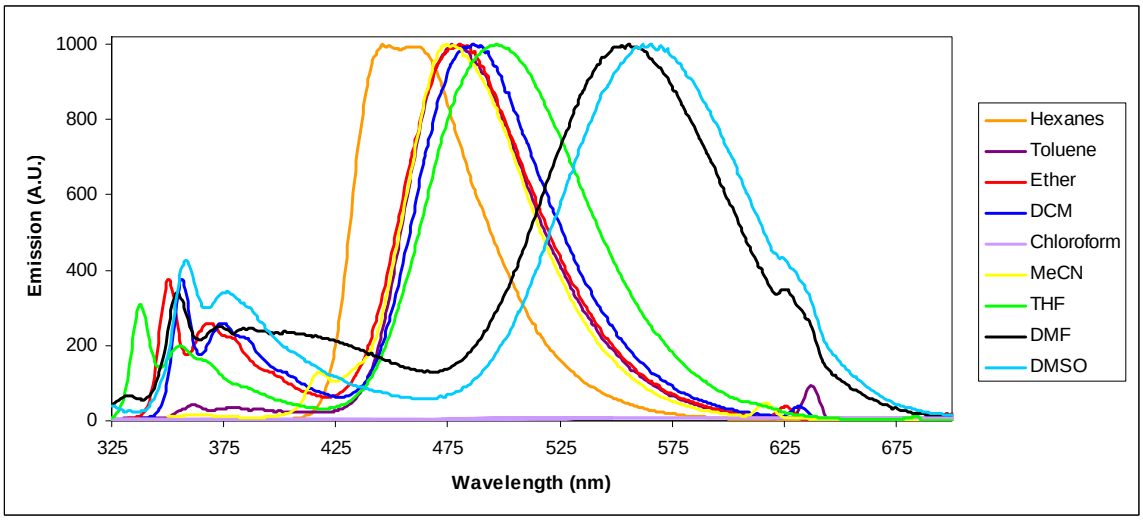
*Plot XII: The Absorbance spectra of compound **1** in various solvents are plotted.*



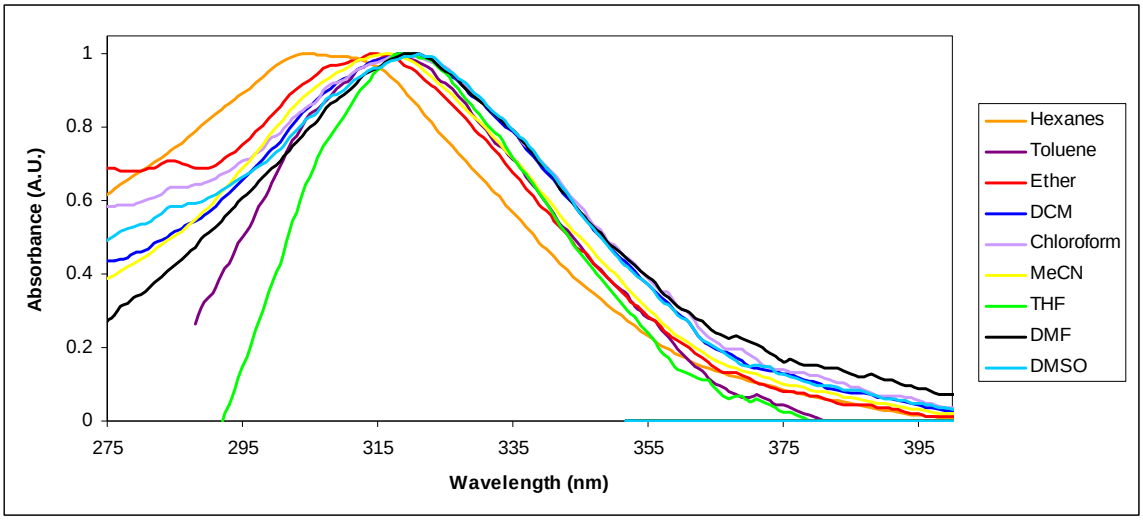
*Plot XIII: The emission spectra of compound **1** in various solvents are plotted.*



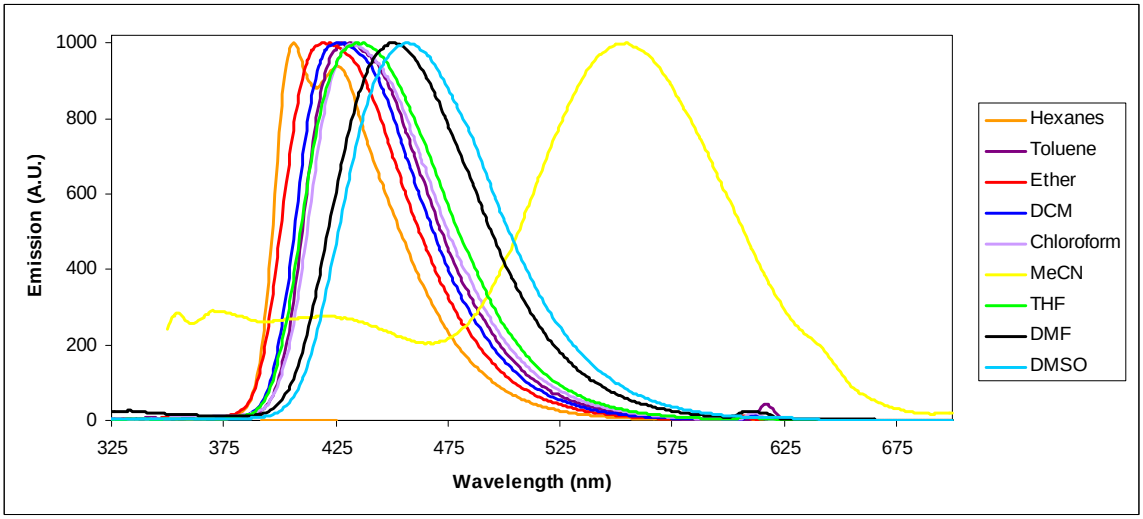
*Plot XIV: The Absorbance spectra of compound **3** in various solvents are plotted.*



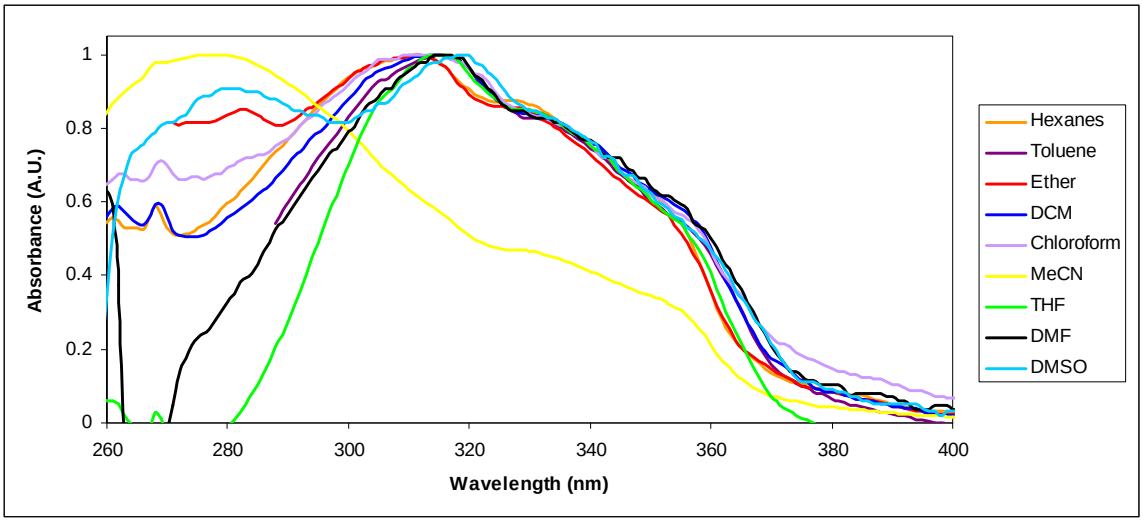
*Plot XV: The emission spectra of compound **3** in various solvents are plotted*



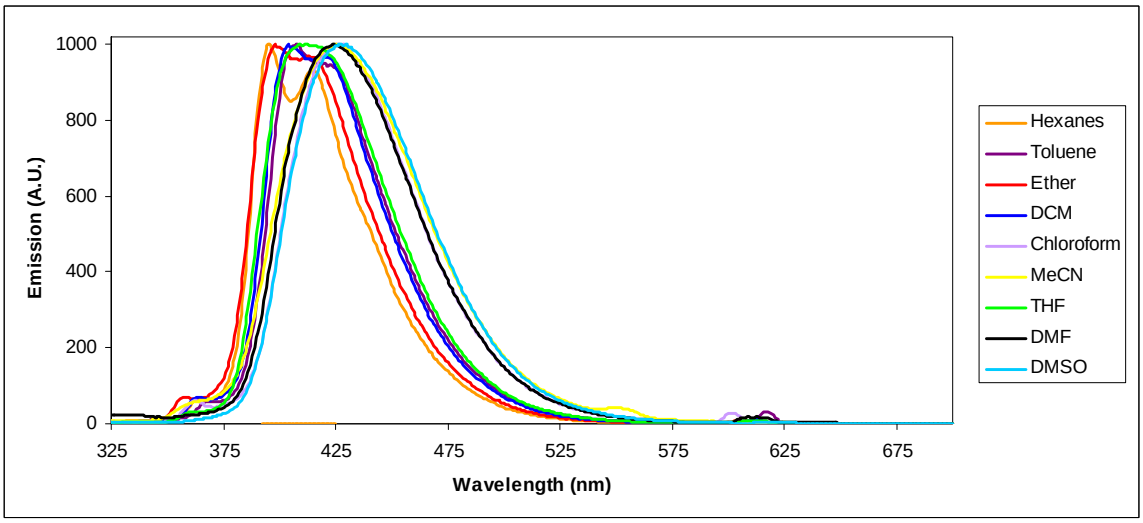
*Plot XVI: The Absorbance spectra of compound **4** in various solvents are plotted.*



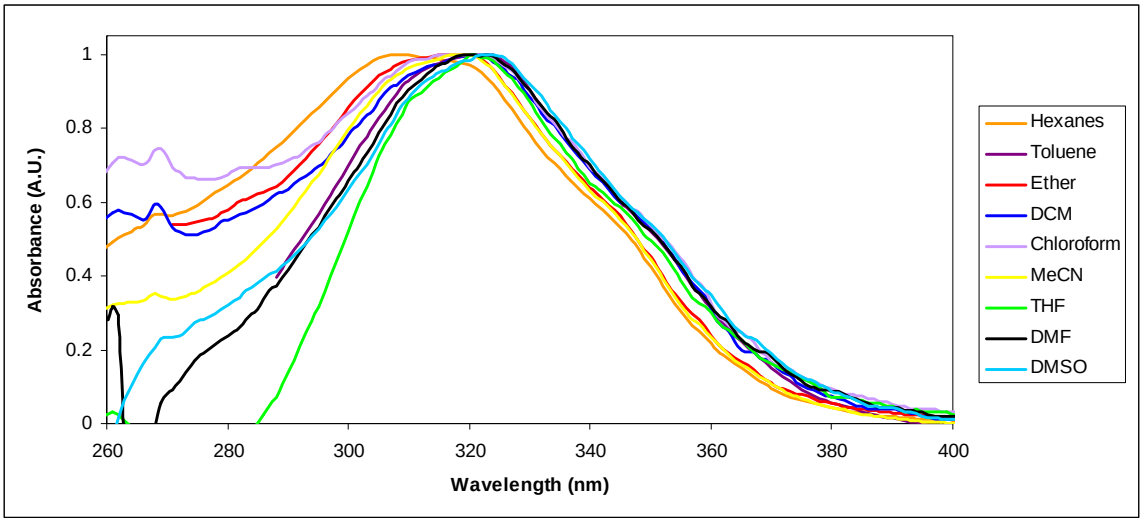
*Plot XVI: The emission spectra of compound **4** in various solvents are plotted*



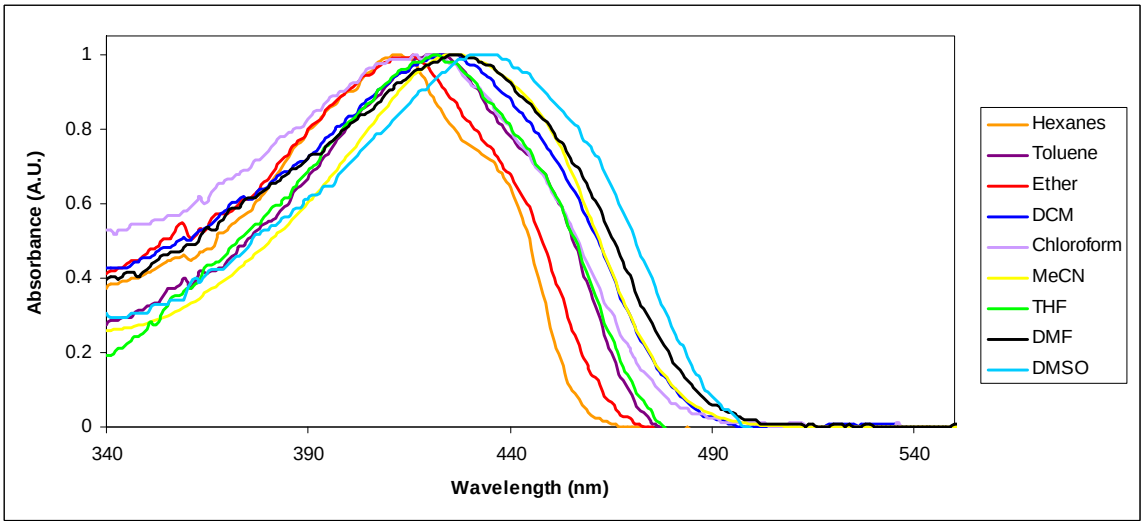
*Plot XVIII: The Absorbance spectra of compound **6** in various solvents are plotted.*



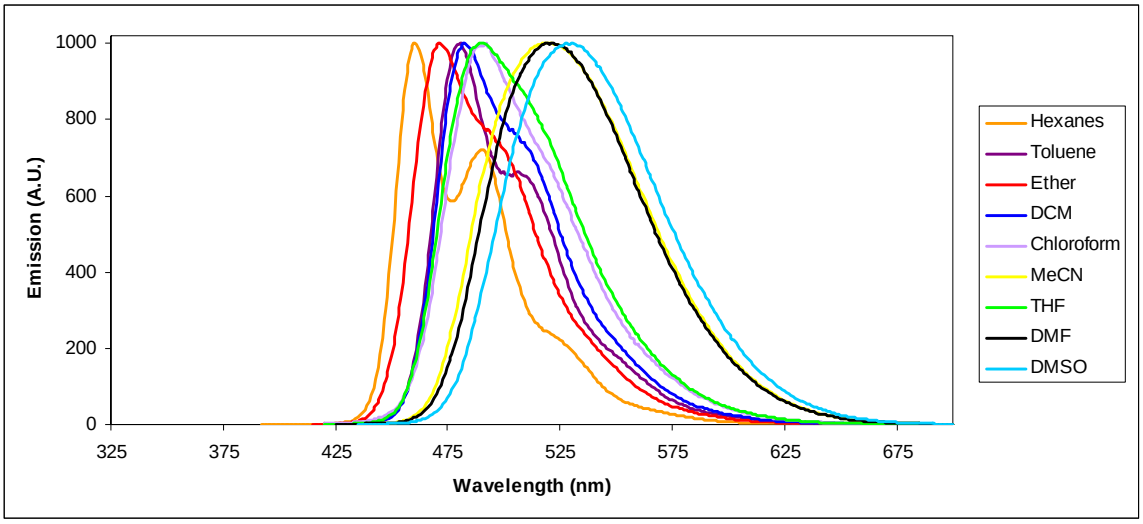
*Plot XIX: The emission spectra of compound **6** in various solvents are plotted*



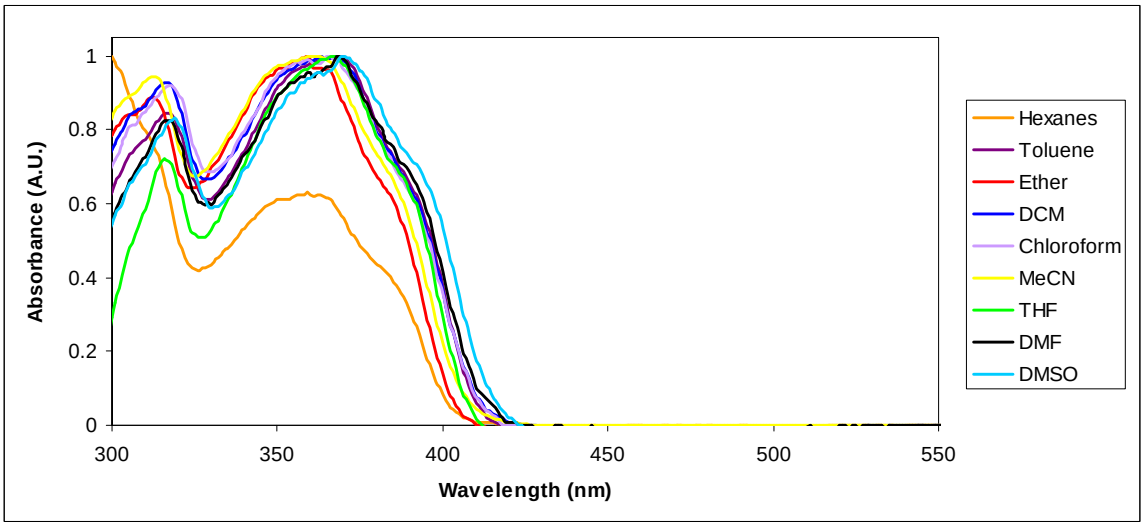
*Plot XX: The Absorbance spectra of compound **7** in various solvents are plotted.*



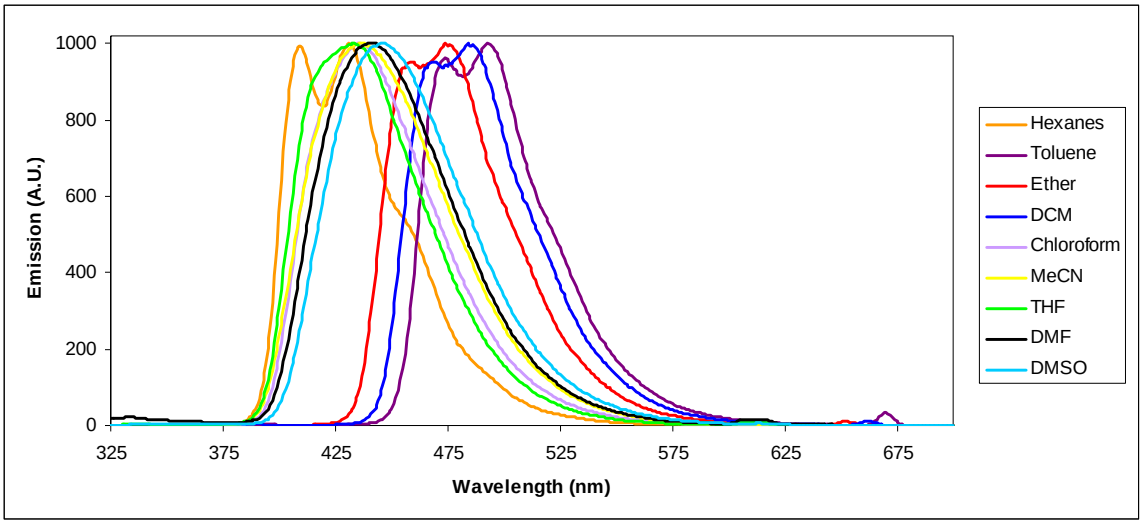
*Plot XXI: The Absorbance spectra of compound **10** in various solvents are plotted.*



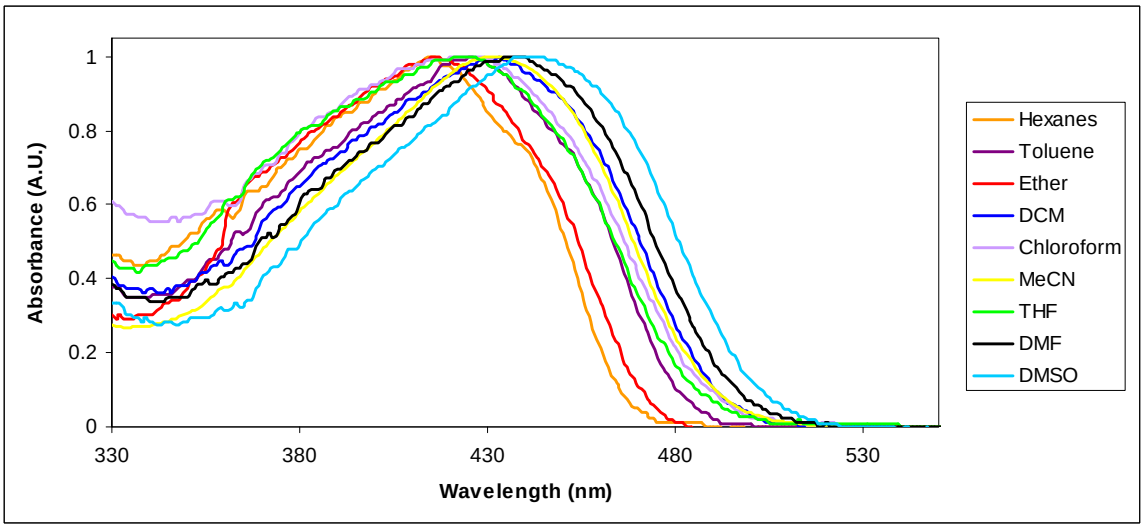
*Plot XXII: The emission spectra of compound **10** in various solvents are plotted*



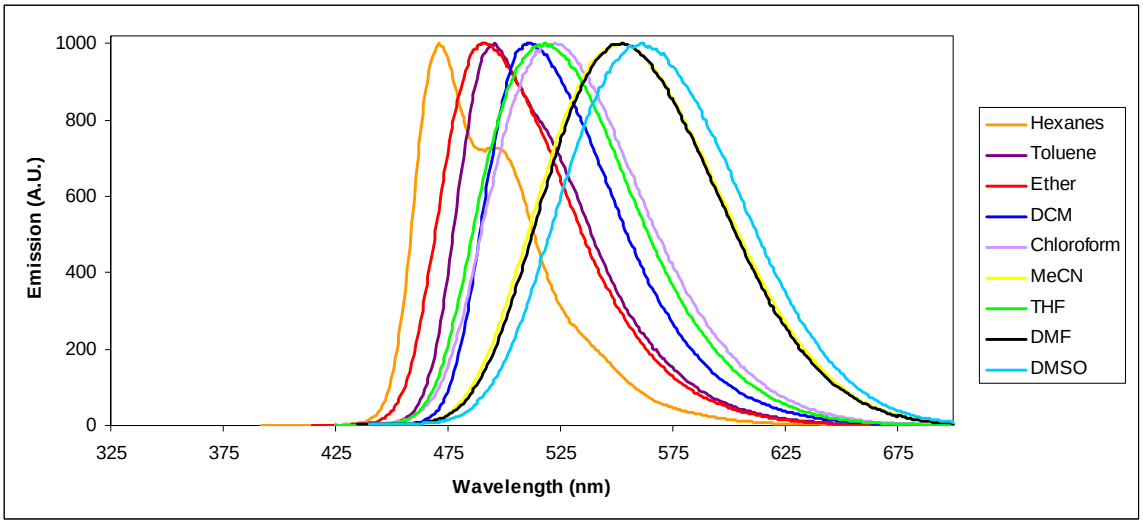
*Plot XXIII: The Absorbance spectra of compound **11** in various solvents are plotted.*



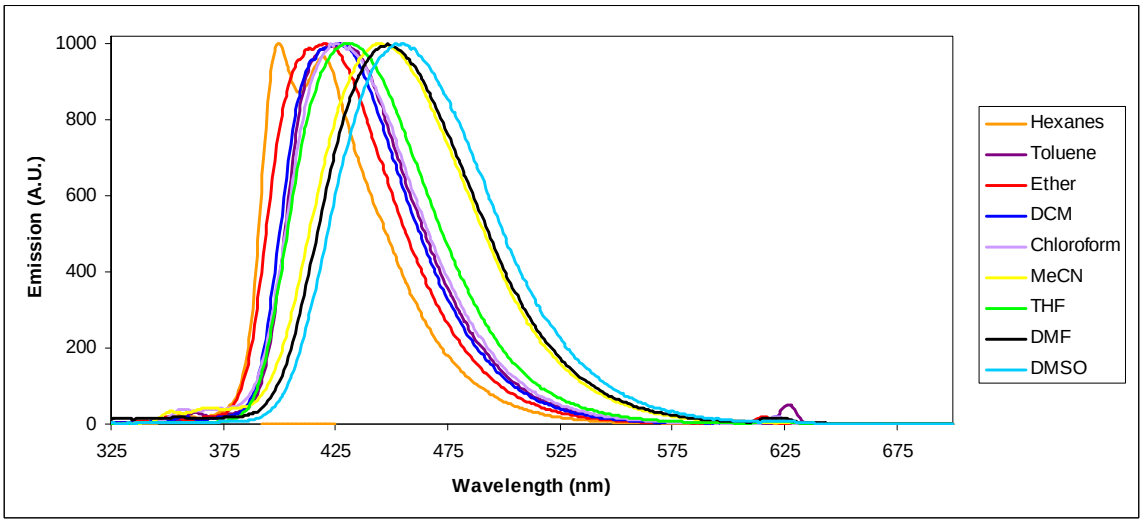
*Plot XIV: The emission spectra of compound **11** in various solvents are plotted*



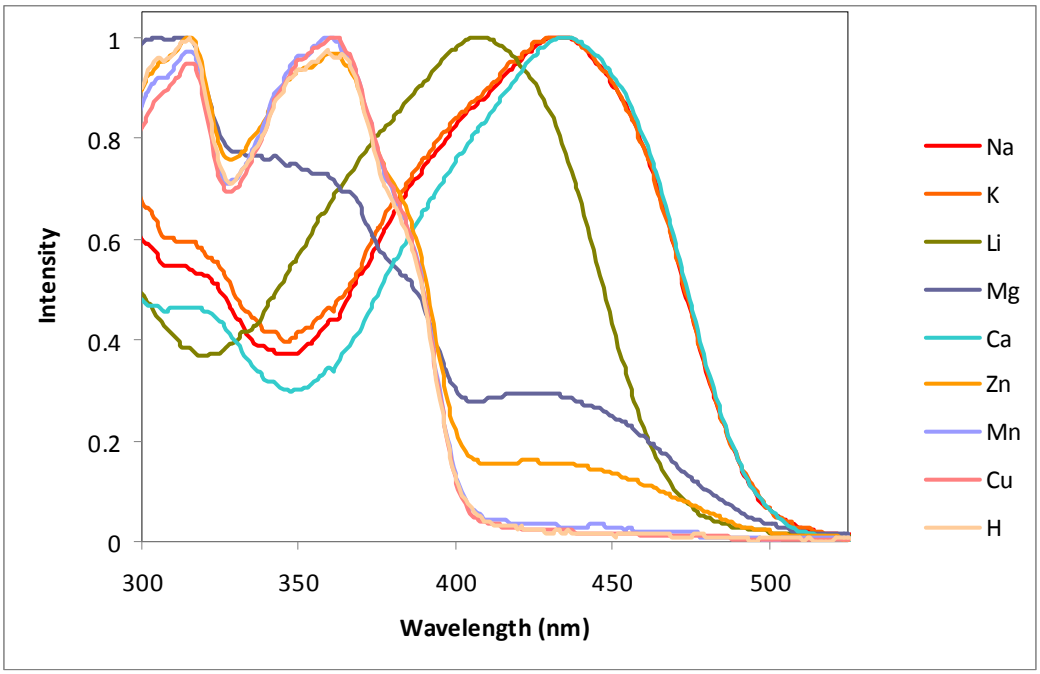
*Plot XXV: The Absorbance spectra of compound **12** in various solvents are plotted.*



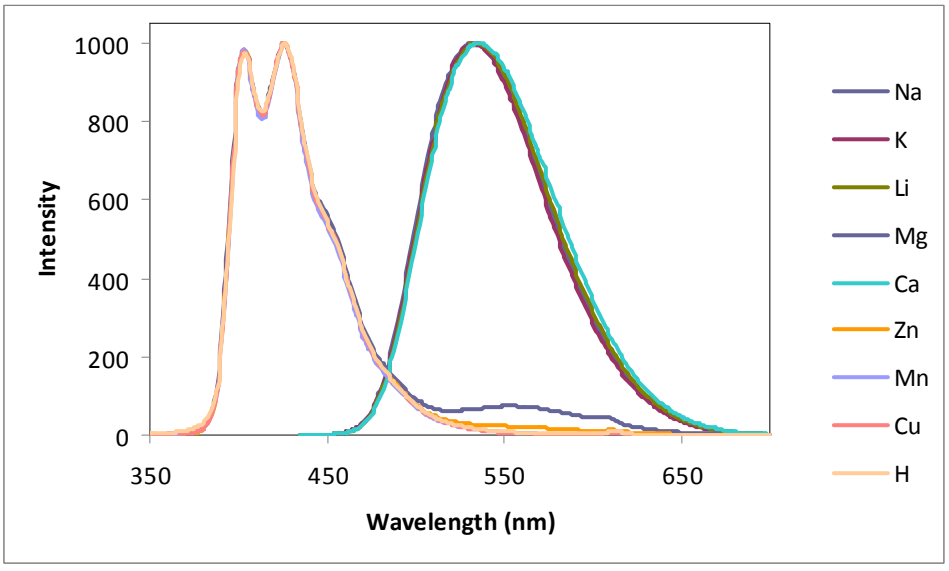
*Plot XXVI: The emission spectra of compound **12** in various solvents are plotted*



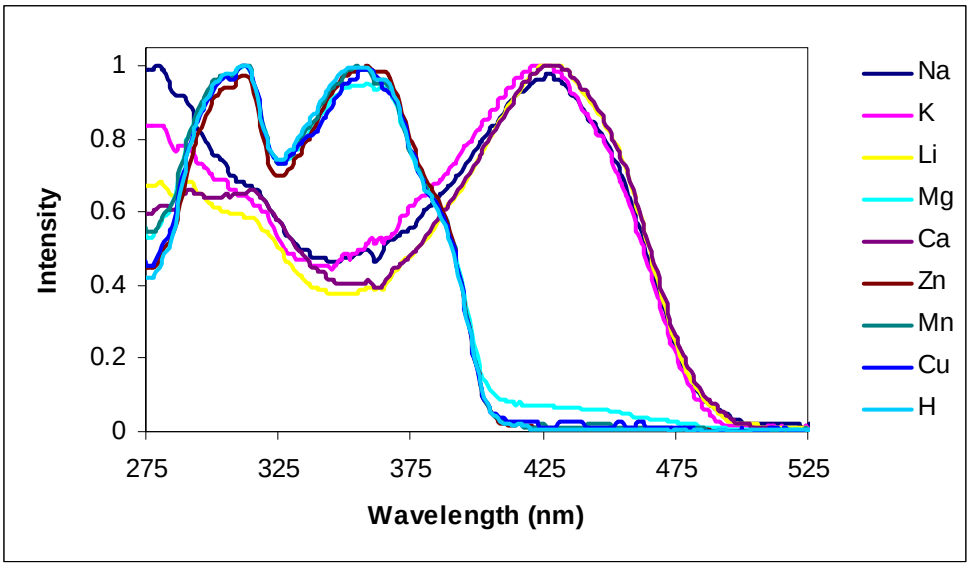
*Plot XVII: The emission spectra of compound **7** in various solvents are plotted*



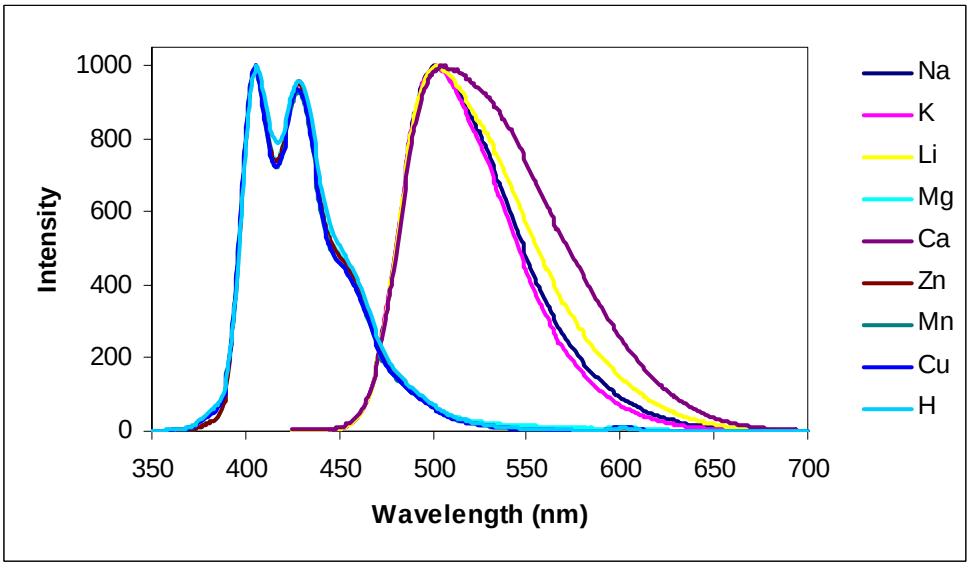
*Plot XXVIII: The Absorbance spectra of compound **9** in various solvents are plotted.*



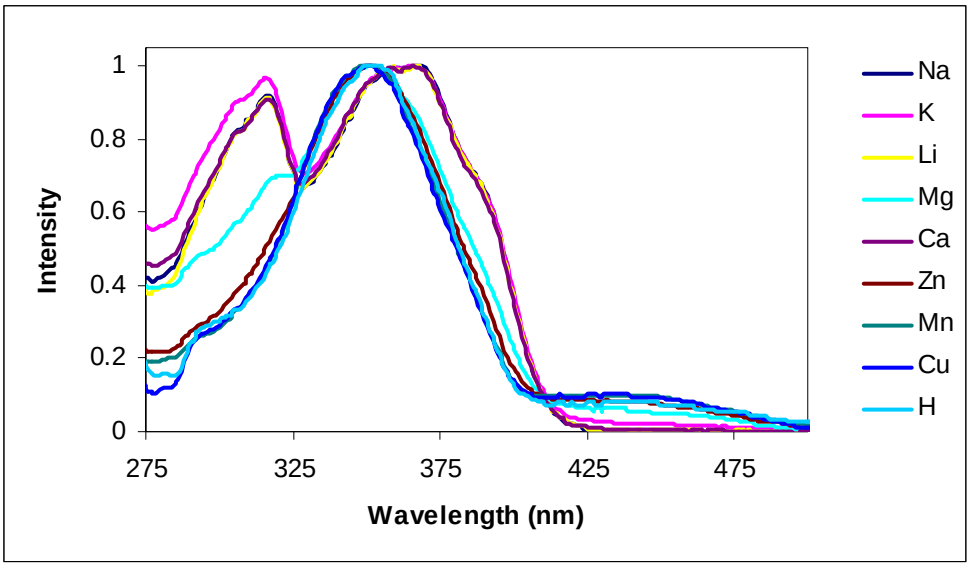
*Plot XXIX: The emission spectra of compound **9** in various solvents are plotted*



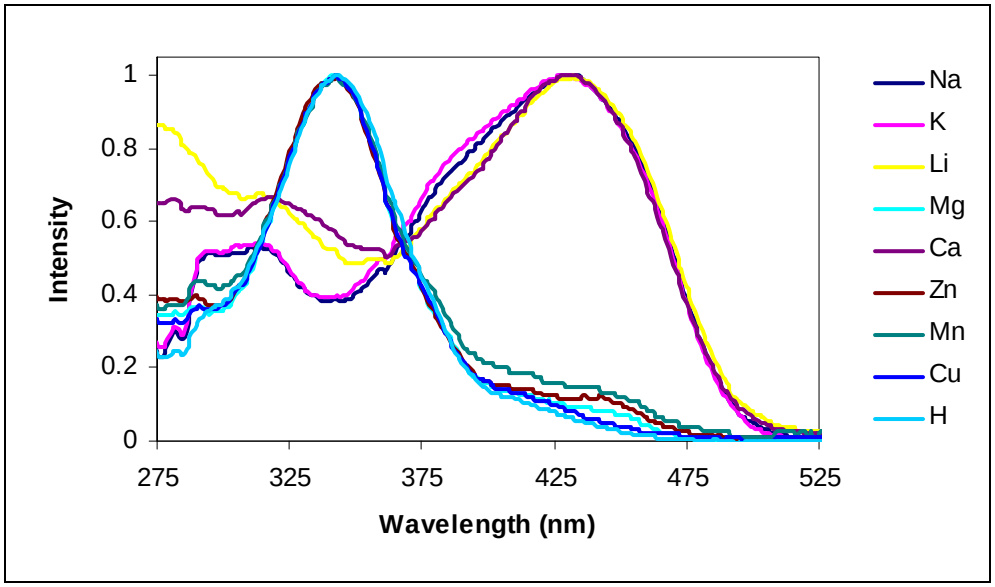
*Plot XXX: The Absorbance spectra of compound **10** in various solvents are plotted.*



*Plot XXXI: The emission spectra of compound **10** in various solvents are plotted*



*Plot XXXII: The Absorbance spectra of compound **11** in various solvents are plotted.*



*Plot XXXIII: The Absorbance spectra of compound **12** in various solvents are plotted.*